Conductive, Lusterless Coatings for Light Metals

Battelle Columbus Laboratories

prepared for

Army Electronics Command

DECEMBER 1972

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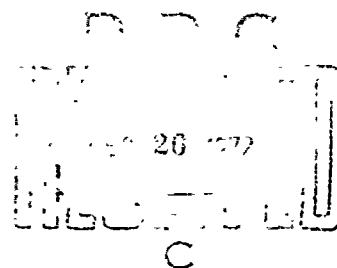Research and Development Technical Report

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CONDUCTIVE, LUSTERLESS COATINGS FOR LIGHT METALS

Final Report

DECEMBER 1972

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BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

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C. H. Layer, G. R. Schaer, J. G. Beach, and W. H. Safranek

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13. ABSTRACT

A metallic conductive, lusterless plating system with improved corrosion durability developed for aluminum on a previous contract was the basis for this program on the improvements of the corrosion durability of magnesium. A composite of electroplates containing either a fused tin or a cobalt-nickel alloy was effective for inhibiting corrosion pits from penetrating through the coating into the magnesium substrates. The efficacy of the coating was not completely demonstrated because of inconsistant quality (adhesion) of copper strike on magnesium, however. A technique proposed for improving the quality of the copper strike includes a cyanide treatment after the application of a zinc displacement coating on magnesium, to improve the adhesion of the subsequent copper strike.

-1a-

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Plating						
Coating						
Conductive						
Lusterless						
Abrasion Resistance						
Corrosion Resistance						
Adhesion						
Flexibility						
Magnesium						
Electroplating						
Nickel Plating						
Porous-Nickel Plating						
Conductive Coating						

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BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

For
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U. S. ARMY ELECTRONICS COMMAND
FORT MONMOUTH, NEW JERSEY

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FOR LIGHT METALS

by

C. H. Layer, G. R. Schaer, J. G. Beach,
and W. H. Safranek

STATEMENT OF THE PROBLEM

The objective of this program was to identify a suitable plating system for improving the durability of magnesium substrates coated with metallic conductive, lusterless electroplates. Common plating practices do not provide corrosion protection comparable with the protection obtained with electroplated aluminum or steel substrates. Magnesium is more active and corrodes rapidly when corrosion pitting of the coating reaches the magnesium substrate or when the coating is mechanically damaged.

The procedure for applying the conductive-lusterless coating over the corrosion resistant electroplated system was identified in a previous program, "Conductive-Lusterless Coatings for Light Metals", conducted under Contract DAAB07-69-C-0360. Development of this procedure was not part of this program. The complete system was governed by the Technical Guidelines, dated July 27, 1971, for conductive-lusterless coatings for light metals.

BACKGROUND AND APPROACH
TO THE PROBLEM

The overall objective of this program was the same as that for the program conducted under Contract DAAB07-69-C-0360, namely to improve conductive-lusterless coatings for light metals. Under the previous contract, a new process for plating conductive lusterless metal was developed and a method for plating nickel on aluminum with no intermediate metal coating was identified. This report discusses the results of investigating methods for applying the conductive-lusterless coating on magnesium. Specifically the objective was to improve the corrosion durability of plated coatings on magnesium.

A protective coating for magnesium must resist both mechanical damage and corrosion pitting. Current recommended procedures for protecting magnesium substrates call for up to 0.002 inch of dense nickel in addition to about 0.0005 inch of a copper undercoating.

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To insure long life, protective coatings should be applied in a way to provide a corrosion barrier, which must be free from pores and have no continuous sites of potential corrosion extending through the coatings. With some methods for applying multilayer electroplates active sites for corrosion pitting are interrupted at the interface between metals. A fused-tin coating which is free of pores or corrosion sites that could form a continuous path from the substrate to the surface is an example of such a coating. Pores in tin deposits are sealed by flowing or fusing the coating. The structure after fusion disrupts any tendency to transmit continuous corrosion sites through the tin layer.

A multilayer system consisting of alternate layers of electrochemically active and passive metals is another example of a system which resists corrosion pitting. The active metal supplies cathodic protection to the adjacent passive metals. Alternating nickel and cobalt electroplates exemplify a system that was expected to be useful for preventing corrosion pitting and resisting mechanical damage.

Another candidate for avoiding continuous corrosion sites is an alloy coating containing a large percentage of intermetallic compounds. Such alloys are generally less subject to corrosion than solid solution alloys because the valence electron imbalance in the solid solutions is partly satisfied by the intermetallic structure. Examples of alloys which contain significant percentages of intermetallic compounds and which may improve the corrosion protection of coatings on magnesium are tin-nickel and bronze alloys.

Examples of systems of multilayer electroplates considered in this program for enhancing the corrosion protection of magnesium are given in Table 1. Each of the concepts discussed above are represented in this list.

The experimental program was directed towards identifying a processing sequence that would provide improved protective and nonreflective coatings for magnesium die castings and wrought alloys. The coating process and the program were divided into three parts as follows:

(1) Investigate procedures for applying metallic coatings adherently.

(2) Study coating systems capable of providing improved resistance to corrosion.

(3) Evaluate systems from Part (2), combined with the conductive, lusterless coating, for meeting USAECOM requirements.

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TABLE I. SYSTEMS OF MULTILAYER ELECTROPLATES

System	Coating Materials and Coating Thickness, mils[a]			
	1	2	3	4

(1) Electroplates Incorporating a Corrosion Barrier Lamina

System	1	2	3	4
A	Sn, 0.25	Watts Ni, 1		
B	Sn, 0.25	Watts Ni, 0.5	SBNi, 0.5[b]	Watts Ni, 0.5
C	SBNi, 0.5	Sn, 0.25		
D	SBNi, 0.5	Sn, 0.25	Watts Ni, 0.5	
E	Watts Ni, 0.5	Sn, 0.25	Watts Ni, 0.5	
F	Watts Ni, 0.5	SBNi, 0.5	Sn, 0.25	
G	Watts Ni, 1	Sn, 0.25		

(2) Electroplates Incorporating One or More Laminae Which Corrode Sacrifically

System	1	2	3
A	Watts Ni, 1	SBNi, 1	
B	SBNi, 1	Watts Ni, 1	
C	Watts Ni, 0.5	Cd, 1	Watts Ni, 0.5
D	Watts Ni, 0.5	Co, 0.5	Watts Ni, 0.5
E	Watts Ni, 0.5	Co-Ni Alloy, 0.5	Watts Ni, 0.5

(3) Electroplates Which Retard Corrosion Because of High Polarization

System	1	2
A	Watts Ni, 2	Pb, 0.5
B	Watts Ni, 2	Pb, 1
C	Watts Ni, 1	Ni-Sn Alloy, 2
D	Watts Ni, 2	Ni-Sn Alloy, 1
E	Watts Ni, 1	Ni-Sn Alloy, 1
F	Watts Ni, 1	Bronze, 1

(a) Chemical symbols are used for the respective metal electroplates.

(b) SBNi = Semibright nickel containing 0.025 percent sulfur.

EXPERIMENTAL PROCEDURES AND RESULTS*

Task 1. Investigation of Procedures for Applying
Metallic Coatings Adherently

The only commercially used system for electroplating magnesium alloys includes zinc displacement and copper electroplated coatings. This system was used as a basis for comparing adhesion obtained by alternate experimental methods. Because of the chemical activity of magnesium and its alloys, only a few electrochemical systems are suitable for conditioning the alloy and depositing adherent electroplates.

Investigation of Displacement Coatings
on Magnesium

The durability of electroplated hardware is influenced by the adhesion and freedom from pin holes of the initial metal coating. Poor adhesion associated with blistering can crack the protective coating and expose the substrate to the corrosive environment. Pin holes in the first coating can initiate pores which tend to propagate in subsequent coatings or induce sites at which corrosive solutions can penetrate at an accelerated rate. Displacement zinc coatings on magnesium are porous, so alternative displacement coatings for magnesium were investigated. The alternatives included antimony, manganese, tin, and zinc alloys. Antimony and manganese were of interest, because antimony is less active than zinc and manganese is more active. Tin was of interest because a process had already been developed for applying tin on magnesium by a displacement reaction. Zinc alloys were included in the investigation because displacement coating of zinc on aluminum are more adherent and less porous when other metals are alloyed with the zinc.

Antimony. An antimony citrate bath was checked and found to attack magnesium with considerable gassing. An adherent deposit of antimony metal was not obtained. Compositions of this and all other solutions are detailed in Appendix A.

Manganese. Metallic displacement coatings on magnesium alloys were formed from two solutions. With a manganese sulfate concentration of 40 g/l at a pH of 4.5 to 5.2, a thin metallic coating was deposited. No coating was apparent when the pH was raised above about 5.2. Displacement coatings were also formed in manganese pyrophosphate solutions with fluoride ions added as a corrosion

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* Experimental data and results are recorded in BCL Record Books 28153, 28167, and 29669.

inhibitor. However, the manganese was too active during exposure to cyanide solutions during attempts to deposit an adherent overlay. Based on this study, there was no advantage for applying manganese in place of zinc.

Tin. Uniform coatings were applied to magnesium alloys when the stannate immersion coating process[*] was checked. However, all attempts to deposit a sound adherent copper, or nickel electroplate over the tin containing coating were unsuccessful. The fluoride modified copper cyanide bath recommended for plating copper on magnesium and an alkaline nickel pyrophosphate bath were evaluated. All deposits were nonadherent. Even an air blast used to dry the panels was often sufficient to lift and peel the metal coating.

Although suitably conductive for electroplating, the displacement tin coating was unsuitable for electroplating copper or nickel adherently. The treatment was developed as a base for paint coatings and is reported to produce a coating of tin and magnesium stannate.

Zinc Alloys. The results of adding salts of manganese, nickel, copper, and tin to a zinc pyrophosphate displacement coating bath also were discouraging. When each of these metal salts, (manganese sulfate, nickel sulfate, copper pyrophosphate, or tin pyrophosphate) were added, the displacement coatings formed on cleaned and activated magnesium alloys were not adherent.

Nickel. Direct application of nickel by electrolytic and electroless deposition was evaluated during a previous contract, DAAB07-69-C-0360,[**] with no indications of improved corrosion durability compared to the composite of zinc, copper, and nickel electroplates.

Procedure for Plating Magnesium Alloys

Because no better alternative procedure was identified for depositing metal on magnesium alloys, the conventional[***] procedure was adopted. It consisted of activation, zinc displacement coating in a pyrophosphate solution, and copper plating in an alkaline cyanide solution before the application of any subsequent plated coatings. The process and solution composition are detailed in Appendix B. Considerable difficulties were encountered with blistering while depositing the experimental protective coatings and the conductive-lusterless metal on magnesium panels. When blistering occurred, the copper separated from the zinc or the zinc from the magnesium interface.

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[*] DeLong, H. K., _Metal Finishing Guidebook and Directory_, Metals and Plastics Publications, Inc., Westwood, New Jersey (1972) page 563.

[**] ECOM 0360-F Report on "Conductive, Lusterless Coatings for Light Metals", October 1971.

[***] Ibid, pp 228-236.

The conventional procedure includes pickling in one of several alternative acid solutions. However, more reproducible results were obtained when abrasive cleaning was used instead of chemical pickling. Wrought panels of AZ31B alloy were cleaned by scrubbing with a brush, water and powdered pumice until all the original surface texture was removed, which also removed the ink identification marking on the sheet stock. Cast panels of AZ91 were cleaned and abraded to remove surface defects by vibratory finishing.

The zinc displacement solution produced adherent zinc coatings when the pH was maintained within the recommended values of 9.6 to 9.9, except when the solution was contaminated with chromic acid by drag-in from the chromic acid pickle.

Adherent, blister-free copper plates were not obtained on the zinc displacement coatings when the recommended copper strike compositions were used with the recommended free-cyanide contents of 7.5 g/l in the fluoride modified copper strike or 5.6 g/l in the Rochelle salt copper strike bath. Blistering was greatly reduced when the free cyanide was raised to 10 to 12 g/l. However, it was necessary to plate the copper at about 8 amp/ft^2 to avoid blistering. The use of this low current density is recommended in published procedures for plating on magnesium.[*] However, such a low current density is inconsistent with procedures for plating on zinc, zinc die castings, and zinc displacement coatings on aluminum.

A modified procedure examined at the end of the experimental work period could be the basis for an improved plating process on magnesium alloy. When an alkaline cyanide dip for 60 seconds containing 5 g/l each of sodium cyanide and sodium hydroxide was used between the zinc displacement coating step and the copper cyanide plating step, copper plates free of blisters were applied at 30 amp/ft^2. The reason for this apparent improvement in platability of zinc coated magnesium is not clear, but it appears that zinc pyrophosphate remaining on the displacement zinc coating is precipitated when the surface is subsequently rinsed free of excess alkaline compounds by water rinsing. The alkaline-cyanide dip apparently redissolves any salts from the surface and conditions the zinc to promote an adherent copper plate at conventional plating current densities. By copper-cyanide plating at low current densities without using the alkaline cyanide dip the zinc salts are slowly dissolved. If higher current densities are used, the salts are entrapped on

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* DeLong, H. K., "Plating on Magnesium By Electrodeposition and Chemical Reduction Methods", Annual Technical Proceeding American Electroplaters' Society, Inc., (1961).

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the surface and result in blistering. This hypothesis is consistent with the improved results obtained when the free cyanide was increased in the copper bath. Increasing the free cyanide would increase the rate of solution of the zinc pyrophosphate salt film.

Blistering can also occur during or after the conductive-lusterless coating (porous nickel) is applied. Because tne bath for applying the porous nickel operates at a ph of about 2.0, chemical attack of magnesium can take place at rack marks if bare magnesium is exposed. Two techniques evaluated for covering bare contact spots are described in the next section of this report.

Coating Over Rack Marks

A successful protective system for magnesium requires complete coverage of all surfaces because any bare areas adjacent to a noble metal corrode rapidly in corrosive atmospheres. Therefore, electrical contact points (rack marks) must be covered. To accomplish this, parts must be reracked during the plating operation. The depositions and fusion of a tin coating was checked as a means of covering the contact spots left after copper plating by the procedure outlined in Appendix B. The fused-tin coating was effective for covering small pores in the coating associated with surface imperfections in the substrate, but did not flow across large 1/4-inch wide bare contact marks.

A multilayer system of zinc, copper, zinc, and copper also was investigated for covering rack marks. Contact points were changed after the first copper plate. Current was applied during the application of the second zinc coating to insure zinc deposition on the bare magnesium contact areas. Details of the procedure are given in Appendix C.

This treatment sometimes produced a pore-free coating over the original bare contact spots. At other times, blisters developed, which were thought to originate under the initial copper strike plate.

Impregnation of Die Castings

During the course of the program, coatings applied on wrought AZ-31 panels showed fewer defects than coatings on cast AZ-91 panels. Impregnation methods, included in QPL-6869 were considered for decreasing the surface porosity of cast magnesium alloy panels. A two component epoxy system* was the most

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* Two component epoxy filler: one parts by volume Epi-Rez 5077, one part Epi-Cure 856, cured at room temperature for 24 hours. Products of Celanese.

applicable because the castings had only surface defects or pits. Epoxy mixtures were impregnated into the surface porosity and the excess removed by mild abrasion after curing the epoxy. All attempts to deposit adherent plates using the zinc displacement, copper-cyanide strike method were unsuccessful. Blisters formed around each epoxy filled pore. The electroplated coating was not thick enough to bridge the epoxy filled pores. This approach for improving the quality was abandoned.

Task 2. Evaluation of Coating Systems

Corrosion-Rate Measurement Procedure

For evaluating representative candidates listed in Table 1, the electro-chemical-corrosion test consisting of applying a constant anode potential to metallic coatings and measuring the current flow was adopted. This procedure is not only faster than alternative tests, but is also more definitive. The product of current and time is a direct measurement of anodic corrosion in a given environment. Examination of the metallic surface after 10 to 60 minutes of polarization will differentiate general (lateral) from pit-type corrosion. The corrosion rate usually varies with time, depending on changes that occur on the surface. For example, an increase in area as a result of pitting tends to increase the rate. The formation of insoluble films invariably increases resistance and reduces the corrosion rate.

Because information on the corrosion of relatively thin metallic coatings in a composite of electroplates was desired and because the potential difference between alternate layers is relatively constant in a given environment, the potentiostatic method was preferred to galvanostatic tests, which measure changes in potential at a constant current density. The corrosion rate is always constant in galvanostatic tests, which are primarily used for examining the tendency for pitting.

A 5-percent sodium chloride solution was selected as the electrolyte for potentiostatic studies because it is believed to be representative of condensation films formed in a marine environment. The pH of the electrolyte was

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adjusted to 3.0 with an addition of acetic acid to accelerate the rate under potentiostatic conditions. This electrolyte has been used in previous studies of this kind.[1-7]
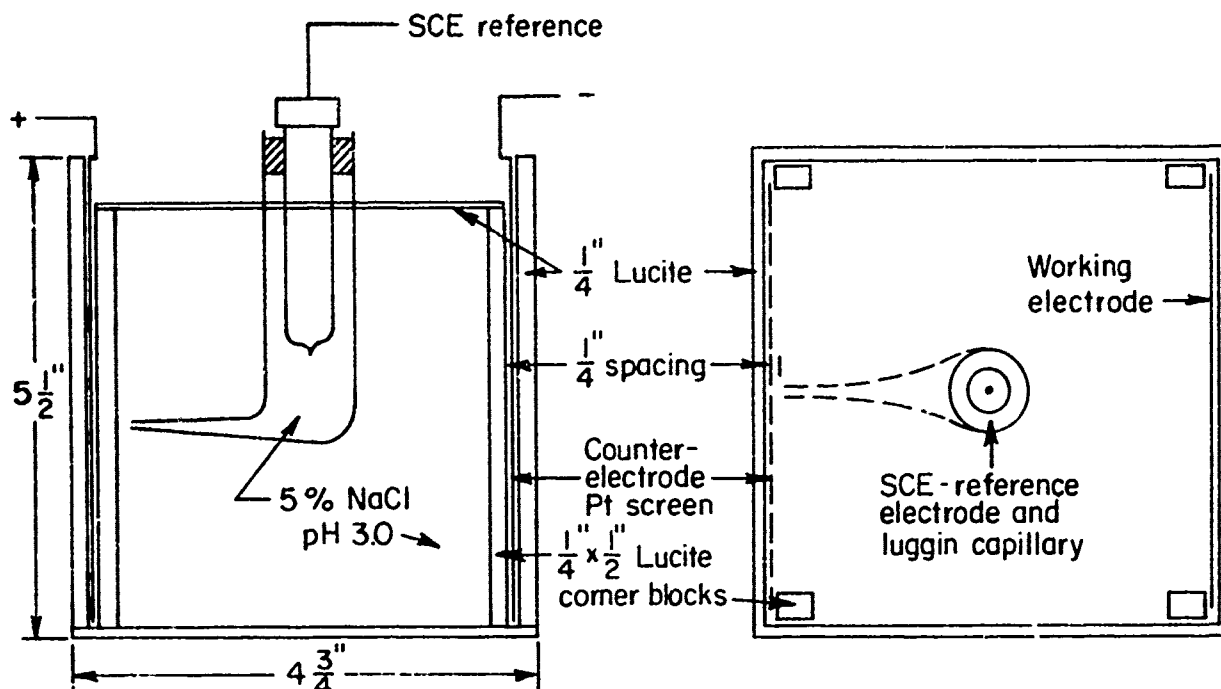
No copper ions were added to the electrolyte because copper depolarizes the cathode reaction when two metals are coupled together. As a result of such depolarization, the corrosion rate is accelerated excessively (ten times, relative to the acidified sodium chloride solution) and accentuates pitting. The copper-free electrolyte was deemed to be more appropriate for developing corrosion rate data for electroplated metals on electronic gear exposed to a marine environment.

An electrolysis cell was constructed from 1/4-inch-thick Lucite with the dimensions shown in Figure 1(a). The electrode distance was 10.0 cm and the volume large enough (1200 ml) to reduce possible effects of concentration changes (metal dissolution and pH). The electrodeposits had an exposed area of 25.0 cm^2 at the center of 10 x 15 cm^2 panels, while the edges and backsides were masked with tape.* The counter electrode was a platinum screen electrode of equal geometric size (5 cm x 5 cm) 20 cm away from the working electrode.

The electrical circuit is shown in the block diagram in Figure 1(b). The potential at the working electrode was controlled by a potentiostat with

(1) Hospadaruk, V., and Petrocelli, J. V., Plating, 48, (5) 479-487 (1961).

(2) Petrocelli, J. V., Hospadaruk, V., and DiBari, S. A., Plating, 49, (1) 50-59 (1962).

(3) Saur, R. L., and Basco, R. P., Plating, 53, (1) 35-38 (1966).

(4) Saur, R. L., and Basco, R. P., Plating, 53, (3) 320-325 (1966).

(5) Saur, R. L., and Basco, R. P., Plating, 53, (8) 981-985 (1966).

(6) Saur, R. L., Plating, 53, (9) 1124 (1966).

(7) Saur, R. L., Plating, 58, (11) 1075-1079 (1971).

* 470 3VEA Tape, product of Minnesota Mining & Manufacturing Company.

SCE reference

+

$5\frac{1}{2}''$

5% NaCl
pH 3.0

$\frac{1}{4}''$ Lucite

$\frac{1}{4}''$ spacing

Counter-
electrode
Pt screen

$\frac{1}{4}'' \times \frac{1}{2}''$ Lucite
corner blocks

$4\frac{3}{4}''$

Working
electrode

SCE-reference
electrode and
luggin capillary

a. Electrolysis Cell

RE = Reference electrode
CE = Counter electrode
WE = Working electrode
RI = Reference input

Cell

RE
CE
WE

RE
CE
WE

A

Potentiostat

RI

Electrometer

Motor
potentiometer

+   −

+
−
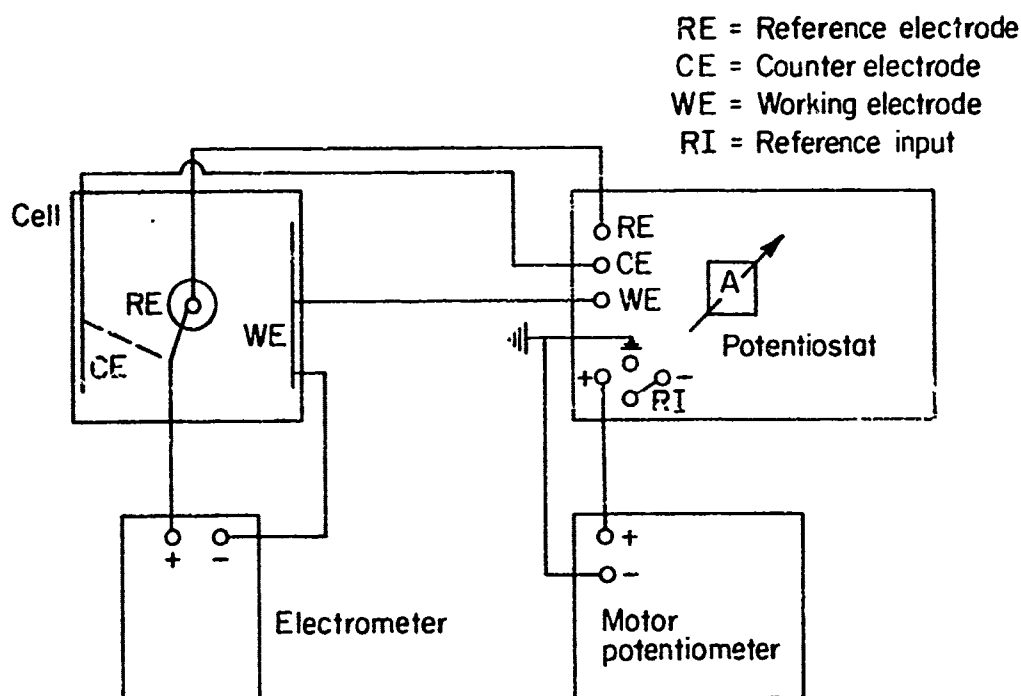
b. Circuitry Block Diagram

FIGURE 1.   EXPERIMENTAL EQUIPMENT FOR MEASURING CORROSION RATES

Potentiostat: Gerhard Bank Elektronik, Goettingen,
W. Germany, Model 6511R
Motor potentiometer: Erwin Halstrup, Goettingen, W. Germany,
Model MP64
Electrometer: Keithley Instruments, Inc., Cleveland, Ohio
Model 610B

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reference to a saturated calomel electrode held approximately 0.5 mm from the
working electrode by a Luggin capillary. Current voltage curves were obtained
by varying the potential from open circuit to 100 mV anodic polarization with
a motor driven potentiometer at a rate of 1000 mV/hr. The currents were indi-
cated by the meter on the potentiostat at 10 mV intervals (every 36 seconds).
The cell voltage was measured with an electronic voltmeter. Current-time data
were obtained by potentiostatic control at 100 mV anodic polarization, noting
current changes during a 60-minute electrolysis period.

The 5-percent sodium-chloride solution was prepared in a 10-liter volume
with analytical reagent chemicals and acidified while stirring with acetic acid
to pH 30. Electrolysis was carried out at room temperature (75 ±5 F). The deposits
were cleaned with magnesium oxide, rinsed in distilled water and 5-percent NaCl,
before immersion into the cell. The solutions and the operating conditions used
for preparing the electrodeposits are summarized in Appendix B.

Corrosion Data

Single Metals. Because the conductive, lusterless nickel is the top
layer in any system for protecting magnesium electronic hardware, the potential-
current relationship of nickel was examined in detail. Figure 2 shows that nickel
is active when its overvoltage potential as an anode is as high as 200 mV. From
200 to 450 mV, high-purity nickel deposited in a Watts-type bath is passive. In
this condition, the corrosion current density was calculated to be less than
25 $\mu amp/cm^2$2.

The rate of corrosion of individual electroplated metals not coupled
with another metal was measure to identify candidates for either sacrificial
or barrier layers that would be useful for delaying corrosion of the magnesium
substrate. The Tafel curves in Figure 3 show that cobalt and semibright nickel
containing 0.025 percent by weight sulfur corrode in acidified sodium chloride
at a faster rate than Watts n' 'el or heat-flowed tin. The corrosion rates for
these metals were as follows:

Watts nickel	2 $\mu amp/cm^2$
Heat-flowed tin	3.3 $\mu amp/cm^2$
Semibright nickel*	4.4 $\mu amp/cm^2$
Copper	6.6 $\mu amp/cm^2$
Cobalt	7.8 $\mu amp/cm^2$

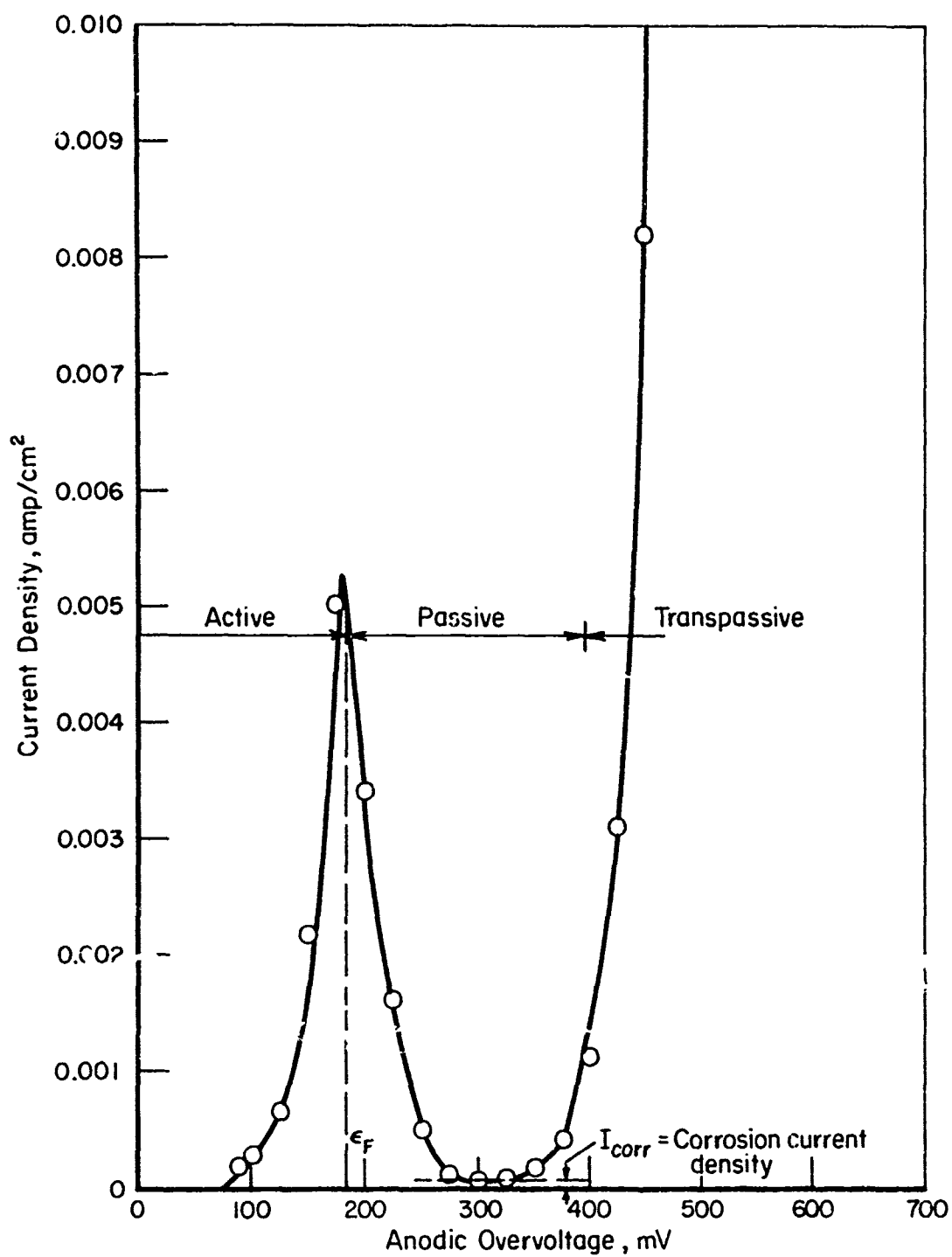* Containing 0.025 percent by weight sulfur.

11

FIGURE 2. CURRENT DENSITY AS A FUNCTION OF POTENTIAL FOR WATTS NICKEL
DEPOSIT IN 5 PERCENT NaCl, pH 3.0, 72 F

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After making the measurements reported in Figure 3, polarization at 100 mV for 60 minutes for the above electrodes showed that semibright nickel and cobalt became very active and dissolved at rates greater than 0.012 amp/cm^2, whereas copper, heat-flowed tin, and Watts nickel were dissolving at rates less than 0.001 amp/cm^2. Visual inspection of the panels at the end of the experiments showed total dissolution of the 0.5-mil cobalt deposit. The semibright nickel corroded laterally starting from the edges of the panel, whereas the 0.5-mil thick Watts nickel exhibited a large number of very small circular corrosion pits. The copper deposits (0.5 mil) corroded uniformly at a very slow rate across the panel. Thus, copper is expected to contribute significantly to the corrosion protection of magnesium alloys. Heat-flowed tin, which corroded slowly under potentiostatic conditions (100 mV) appeared to be a good candidate for a barrier coating.

Composite Metal Deposits. Curves like those in Figure 3 showing current density increases as a function of increasing potential were duplicated for composites of electroplates listed in Table 1, Section (1). The current-potential curves for nickel over tin corresponded closely to the curve for nickel in Figure 3. Similarly, the curve for tin over nickel was about the same as the curve for tin in Figure 3. This agreement indicates that the nickel and tin deposits were nonporous.

Polarization data for up to 60 minutes are shown in Figure 4 for several composites of electroplates. All composites of nickel over tin showed an increase in current density with time, evidently a result of the increase in surface area caused by nickel corrosion pitting. Composites of tin over nickel polarized rapidly, due to oxide film formation. Thus, tin appears to be a good barrier coating between two layers of nickel, in comparison with other systems. The pinhole corrosion through the outer nickel layer will be arrested at the nickel-tin interface because tin polarizes rapidly.

Evaluation of a 50-50 weight percent nickel-cobalt electroplated alloy over different subcoatings is shown in Figure 5. Anodic dissolution at 100-mV polarization indicated a higher corrosion rate for cobalt-nickel alloy than for Watts-nickel, which can be favorable for increasing the lateral corrosion of the sacrificially corroding layer.

CASS Evaluation. AZ31B wrought, and AZ91 die cast panels were plated following the outline of plating procedures in Appendix B. However, the porous nickel overlay was omitted. The panels were then exposed to 16 hours of copper
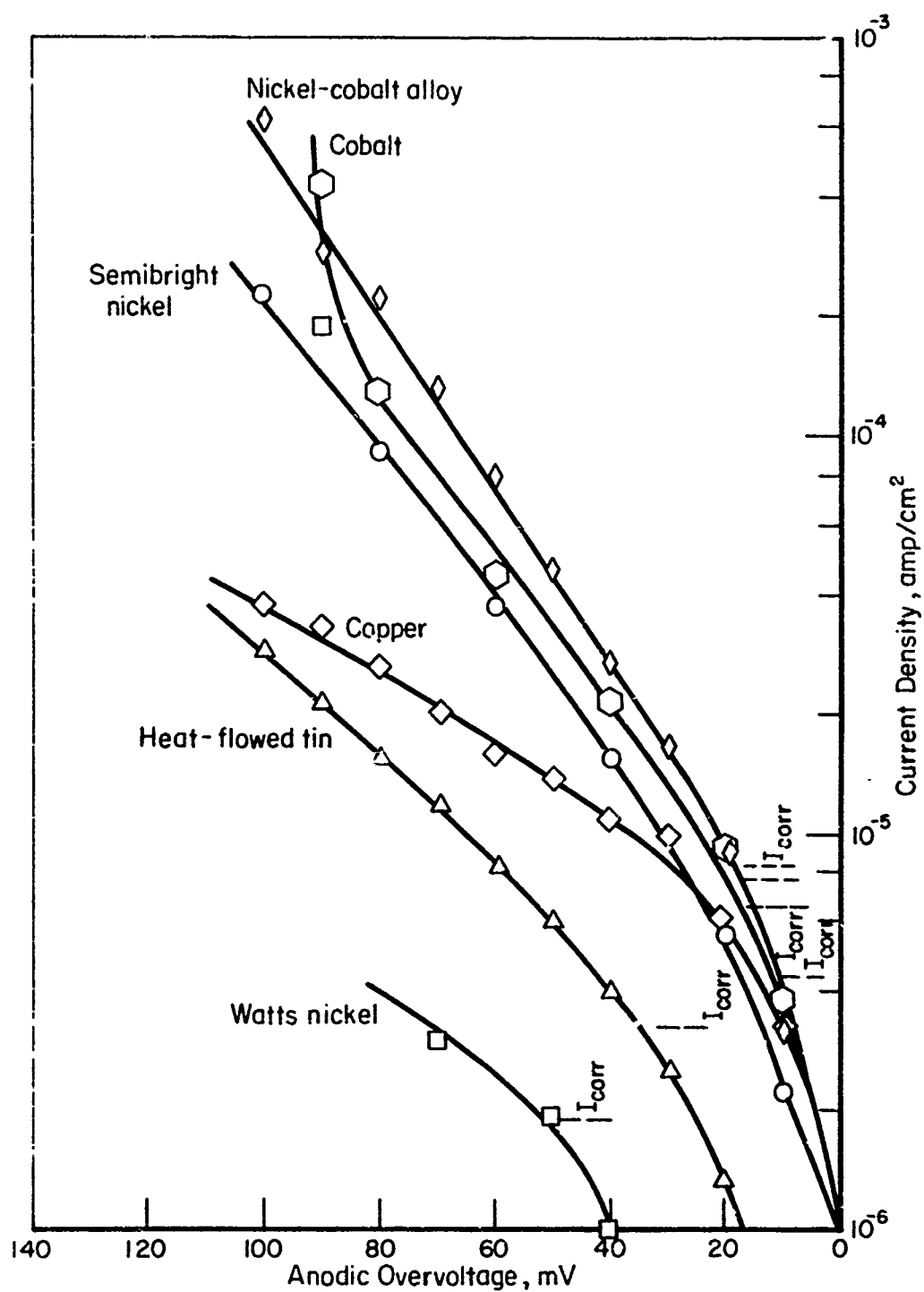
FIGURE 3. ANODIC POLARIZATION OF SINGLE METALS DEPOSITED
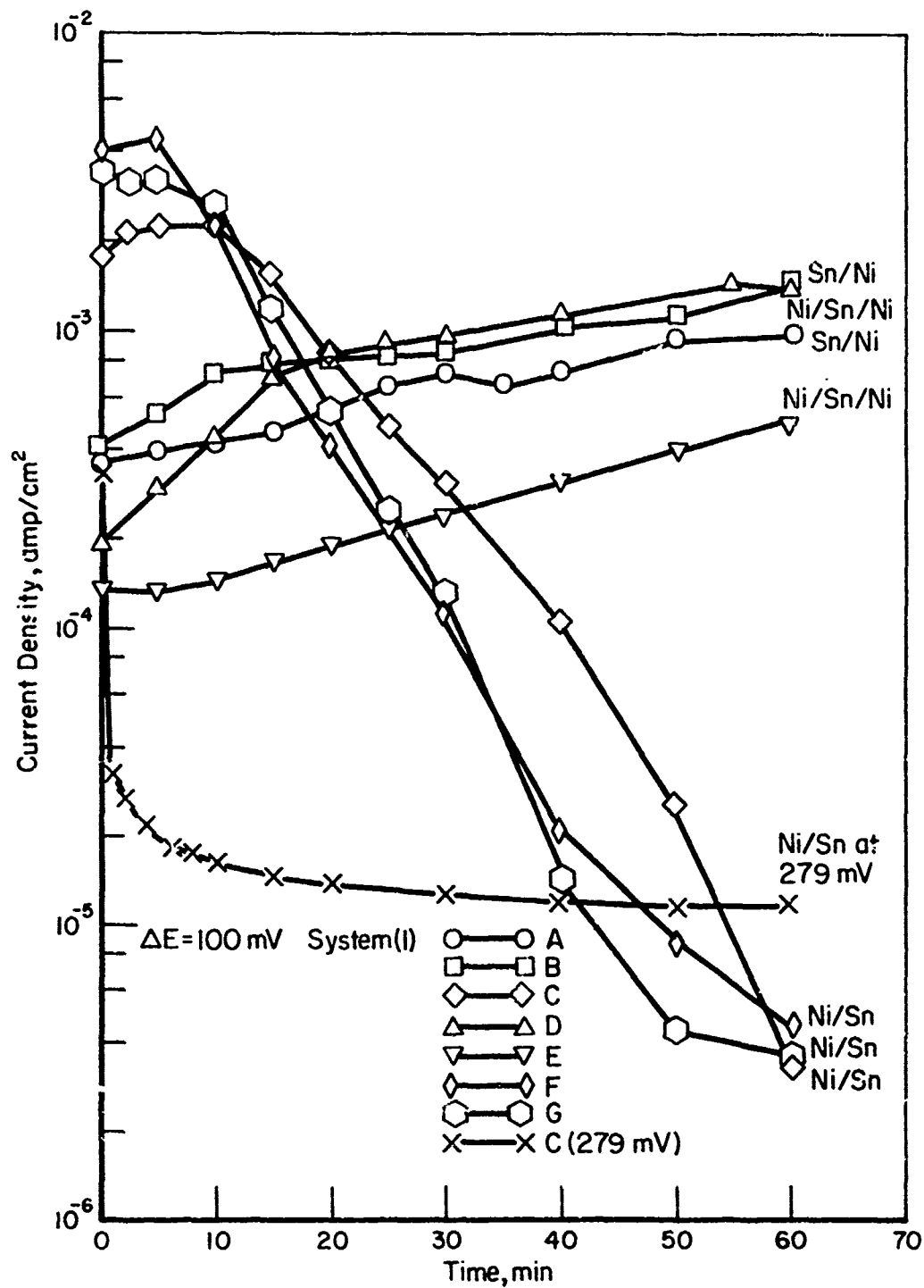ONTO STEEL 5-PERCENT NaCl, pH 3.0

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FIGURE 4. ANODIC POLARIZATION OF COMPOSITE COATINGS, TABLE 1,
SECTION (1), IN 5-PERCENT NaCl, pH 3.0 at 100 mV
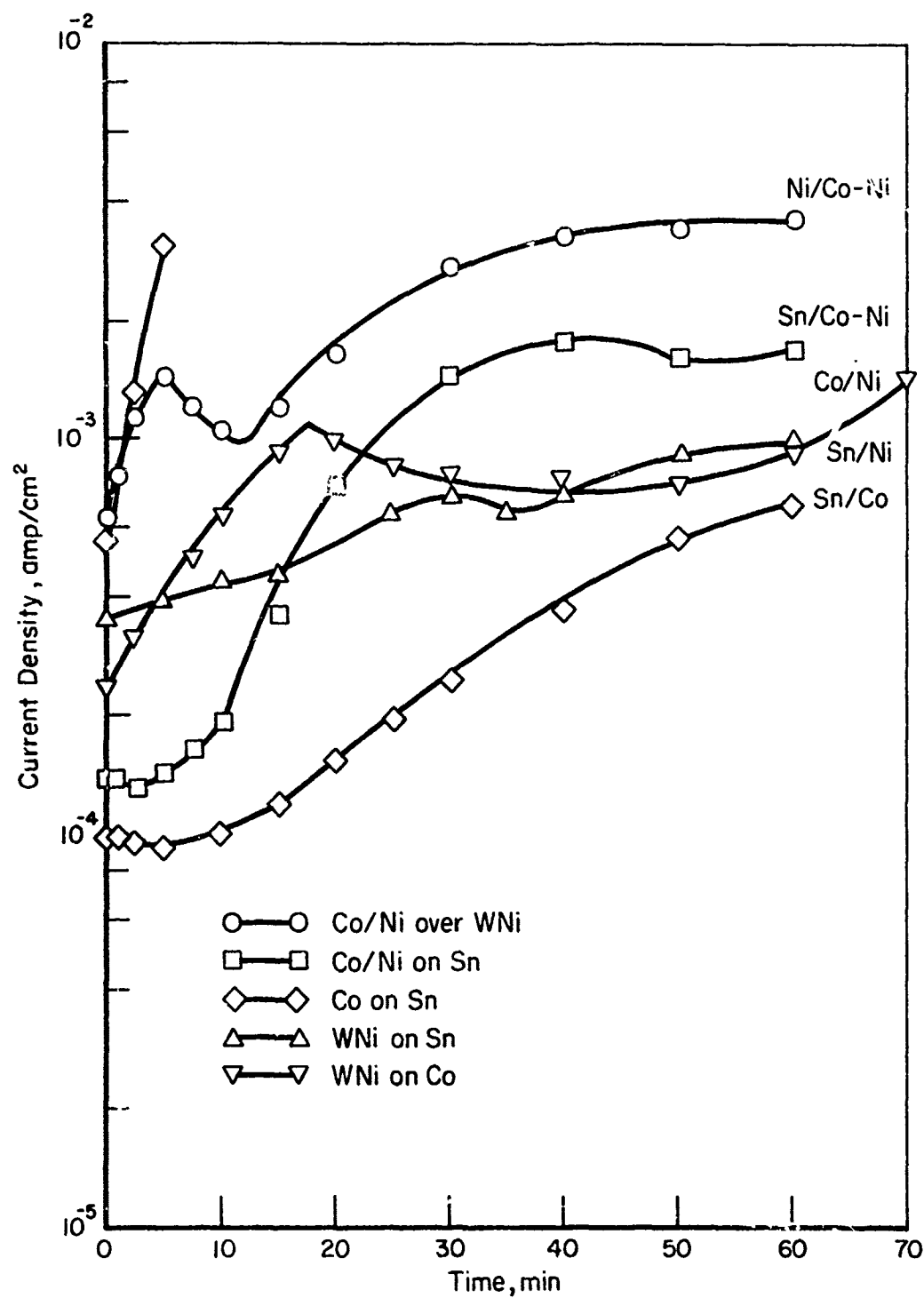ANODIC POLARIZATION

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FIGURE 5. CURRENT-TIME RELATIONSHIPS FOR CORROSION OF NICKEL-COBALT
ALLOY IN 5-PERCENT NaCl, pH 3.0 at 100 mV POLARIZATION

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accelerated acetic acid salt spray (CASS) for 16 hours. The results in Table II show that systems incorporating either heat-flowed tin or cobalt-nickel alloy between two layers of nickel were better corrosion barriers than systems that included an intermediate layer of cobalt or tin-nickel alloy. The promising composites including cobalt-nickel alloy or Watts nickel over tin were further evaluated on wrought and die-cast magensium panels, all of which were plated with porous, lusterless nickel.

Table III shows that both coating systems provided good corrosion protection during exposure to the CASS test and can be expected to withstand the required 96 hours of neutral salt spray. Composites containing Watts nickel underneath the porous coating exhibited slightly better corrosion protection then composites that included cobalt-nickel alloy under the porous nickel. The electroplated wrought alloys had fewer corrosion pits than the plated die-cast alloys, the basic difference originating from magnesium alloy defects.

Evaluation of Bond Strengths

Investigation of bond strengths for composites of electroplates on wrought magnesium panels showed satisfactory results for systems consisting of copper, nickel, cobalt-nickel alloy and nickel. Bend tests showed no evidence of a weak bond at any interface. However, bend tests on panels plated with systems that included an intermediate fused-tin layer revealed a disadvantage that might provoke failures for electronic hardware introduced into field service. When panels were bent to fracture, separation occurred within the tin layer. One layer of tin could be easily peeled from another. This weakness in bond strength was a result of the very low tensile strength (only about 2,000 psi) of the tin.

Because systems including an intermediate corrosion-barrier layer of tin exhibited a weak bond strength in bend tests, the alternative candidate system showing promise for improving the corrosion resistance of electroplated magnesium, which consisted of copper (0.3 mil), nickel (0.5 mil), cobalt-nickel alloy (0.5 mil), nickel (0.5 mil), and porous, lusterless nickel, was selected for supplemental evaluation. The practical aspects of ultilizing this composite of electroplat ¬ were examined by plating four panels at a time in each successive plating bath.

TABLE II.   RESULTS OF EVALUATION OF ELECTROPLATED
MAGNESIUM ALLOYS IN CASS FOR 16 HOURS

| Magnesium Alloy | Coating Metal and Thickness, mil | | | | Number of Corrosion Pits |
	Copper	Watts Nickel	Intermediate Coating	Watts Nickel	
AZ 91[a]	0.3+	0.5	Watts nickel, 0.5	0.5	>50
AZ 31B[b]	"	"	Ditto	"	1
AZ 91	"	"	Semibright nickel, 0.5	"	26
AZ 31B	"	"	Ditto	"	3
AZ 91	"	"	Cobalt, 0.5	"	~40
AZ 31B	"	"	Ditto	"	1
AZ 91	"	"	Co-Ni alloy, 0.5	"	3
AZ 31B	"	"	Ditto	"	1
AZ 91	"	"	Sn-Ni alloy, 0.5	"	15
AZ 31B	"	"	Ditto	'	8
AZ 91	"	"	Heat flowed tin, 0.25	"	0
AZ 31B	"	"	Ditto	"	1

(a)   Panel area was 4 inch x 6 inch.

(b)   Panel area was 4 inch x 4 inch.

TABLE III. RESULTS OF EVALUATION OF ELECTROPLATED MAGNESIUM ALLOYS
FINISHED WITH CONDUCTIVE, LUSTERLESS NICKEL IN CASS

| Coating Metal and Thickness, mil | | | | | | Number of Corrosion Pits | | |
| | | | | | | 16 Hours | | 32 Hours |
Copper	Watts Nickel	Heat Flowed Tin	Watts Nickel	50-50 Co-Ni Alloy	Porous Nickel	AZ 31B	AZ 91	AZ 31B
0.3+	0.5	0.25	0.5	--	0.8	0	0	1
						0	--	1
						1	--	4
0.3+	0.5	0.25	--	0.5	0.8	2	5	2
						2	--	3

Task 3. Plating Panels for Evaluation

Copper, nickel, and cobalt-nickel alloy plating solutions were prepared and 60 to 100-gallon plating tanks were equipped to handle racks holding four panels (4 x 4 inches). The procedure is detailed in Appendix B. Some of the tanks and some of the solutions used during the previous project on Contract DAAB07-69-C-0360, including the porous nickel plating solution developed for applying the final conductive, lusterless coating were also used during this project. When this porous nickel plating solution, which had been concentrated for storage purposes, was diluted to volume, heated and mixed to suspend the activated carbon, the characteristics and properties of the deposit on the first plated panel matched the desired properties obtained on the previous program. Thus, the stability of the bath during idle periods was established.

Proper operation of all treating and plating baths was confirmed first by plating one panel at a time. The deposits duplicated the results obtained in the small tanks adopted during the previous development part of the program. However, inconsistent results were observed when 4 panels at a time were processed; the copper plate sometimes blistered. No pattern was identified for the blistering. Blisters sometimes occurred on none, or all four panels and at different positions on the rack. Rinsing after the application of the zinc displacement coating appeared to be a critical step affecting blistering, but the current applied initially in the cyanide copper strike was also critical. Of more than 200 panels which were plated, only about 20 were obtained in a blister-free condition suitable for further evaluation.

Five panels of AZ91 cast alloy and four of AZ31 wrought alloy plated by Process A in Appendix B were exposed for 120 hours in 5 percent by weight neutral salt spray. From one to five corrosion pits noted on each of the five cast alloy panels after the first 24 hours of exposure were probably caused by magnesium surface porosity which was not completely covered during plating. No additional corrosion pits were seen until after 96 hours. Between 96 hours and 120 hours three of the panels developed one or more new pits through the coating. The edges of some electroplated cast panels also were corroded during the salt-spray test.

Wrought panels of AZ31 alloy were severely corroded at the contact marks on the edges of the panels. Corrosion spread laterally as much as one-half inch. However, no pits through the protective coating were seen on other areas after 120-hours exposure. These results indicate that the composite coating is an efficient corrosion barrier but emphasize the need for complete coverage of magnesium including edges and rack-contact points.

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CONCLUSIONS

Two composites of electroplates were identified which appeared to have prospects for improving the corrosion durability of magnesium hardware plated with the conductive-lusterless coating. These composites of (1) nickel plus heat-flowed tin plus nickel, or (2) nickel plus cobalt-nickel alloy plus nickel, prevented corrosion pitting from penetrating through the coatings into the magnesium alloy substrate during 16 hours of exposure to copper accelerated salt spray (CASS). Composites including a fused layer of tin were mechanically weak, but the system including the cobalt-nickel alloy satisfactorily resisted bend tests with no bond failures. The composite coating system consisting of nickel plus cobalt nickel plus nickel is a good candidate for protecting magnesium because it resisted corrosion pitting. Any pits progressing through the outermost nickel layer to the cobalt alloy were arrested at the interface of the initial nickel layer by the sacrificial potential supplied by the cobalt alloy.

An extensive campaign directed at plating four panels at a time with Composite (2) was not successful in identifying a procedure for avoiding blisters consistently. Blistering occurred under the copper electroplate, applied over zinc coated magnesium. During the last week of the program, improved copper plating was obtained over the zinc displacement coating by using an alkaline cyanide solution soak. The cyanide solution is believed to dissolve precipitated zinc pyrophosphate from the metal surface, which may be the primary cause for blistering.

A process was identified which has prospects for plating a complete envelope free from bare-rack contacts on magnesium panels. With this process, contact positions were changed after the application of the conventional zinc displacement coating and copper strike, and another zinc coating was applied in the same zinc solution using a low current density. A second copper electroplate covered the original contact marks with a coating which was adherent and essentially pore free.

The electroplating bath for applying the conductive-lusterless coating was shown to be stable during idle periods because the expected desired results were obtained with no need for adjustments after the solution had been stored for over 12 months without use.

Attempts to reduce the porosity of electroplates on magnesium alloy casting by filling surface pores with epoxy were unsuccessful.

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RECOMMENDATIONS

The development of an electroplated coating for improving the durability of magnesium should be continued and should include the following objectives:

(1) Improve the activating process following the displacement zinc coating step, prior to the cupper cyanide strike, in order to improve the reliability of the process and the bond between magnesium and the copper electroplate.

(2) Continue the investigation of laminates of nickel-cobalt alloy-nickel electroplates to identify optimum thicknesses and composition of the cobalt alloy for improving corrosion durability.

(3) Continue the investigation of fused-tin coating in laminates with nickel to identify optimum condition for obtaining maximum strengths in the tin layer by complete diffusion alloying of the tin layer.

(4) Continue the investigation of procedures for plating over rack contacts to provide a complete envelope covering for protecting magnesium.

(5) Demonstrate improved corrosion durability of the best coating identified in Item (2) or (3) and (4) combined with the conductive, lusterless coating.

APPENDIX A

<u>SOLUTION COMPOSITIONS INVESTIGATED FOR</u>
<u>APPLYING DISPLACEMENT COATINGS</u>

APPENDIX A

SOLUTION COMPOSITIONS INVESTIGATED FOR
APPLYING DISPLACEMENT COATINGS

The compositions of experimental solutions investigated for applying displacement coatings of antimony, manganese, and tin were as follows:

Antimony Citrate

Potassium citrate	$[K_3C_6H_5O_7 \cdot H_2O]$	145g/ℓ
Citric acid	$[K_3C_6H_5O_7 \cdot H_2O]$	185g/ℓ
Antimony oxide	$[Sb_2O_3]$	60g/ℓ
pH		3.7
Temperature		130 F
Time		5 minutes

Manganese Sulfate

Manganese sulfate	$MnSO_4 \cdot H_2O$	20 to 40g/ℓ
Ammonium sulfate	$(NH_4)_2SO_4$	0 - 20g/ℓ
pH		4.5 - 5.2
Temperature		80 F
Time		5 minutes

Manganese Pyrophosphate

Lithium fluoride	[LiF]	0 - 4g/ℓ
Potassium pyrophosphate	$[K_4P_2O_7 \cdot H_2O]$	200g/ℓ
Manganese sulfate	$[MnSO_4 \cdot H_2O]$	28g/ℓ
pH		5 - 10
Temperature		75 - 120 F
Time		5 minutes

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Potassium Stannate*

Sodium hydroxide [NaOH]	10g/ℓ
Potassium stannate [$K_2SnO_3 \cdot 3H_2O$]	50g/ℓ
Sodium acetate [$NaC_2H_3O_2 \cdot 3H_2O$]	10g/ℓ
Sodium tetrasodium pyrophosphate	
[$Na_4P_2O_7$]	85g/ℓ
pH	12.6 - 13.0
Temperature	180 F
Time	up to 20 minutes

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* License for use of this process available from Mac Dermid Inc., or Dow Metal Products Company.

APPENDIX B

<u>PROCEDURE FOR PLATING PROTECTIVE AND</u>
<u>CONDUCTIVE-LUSTERLESS-COATING ON MAGNESIUM</u>

APPENDIX B

PROCEDURE FOR PLATING PROTECTIVE AND
CONDUCTIVE-LUSTERLESS-COATING ON MAGNESIUM

Procedure A. Incorporating Cobalt-Nickel Alloy Electroplate

This stepwise procedure for plating four 4 x 4-inch panels at a time was as follows:

1.A Die Cast Panels

Vibratory Finish

1.B AZ-31 Sheet

Scrub with powdered pumice and brush to remove ink marking and other surface soils.

2. Soak in alkaline cleaner (Solution A) 7 minutes, 170 ± 5 F.

3. Rinse in tap water in overflowing tank.

4. Soak in activator (Solution B) 1.0 minutes, 85 ± 5 F.

5. Rinse in tap water in overflowing tank.

6. Soak in zinc pyrophosphate solution (Solution C) 7.5 minutes, 177.5 ± 2.5 F, pH 9.6 to 9.9 electrometric.

7. Rinse in tap water in overflowing tank.

8. Copper plate (Solution D)

Enter with current on 18 minutes, 8.5 amps/ft^2, 127 ± 2 F, pH 10.0 to 10.4 electrometric.

9. Rerack to change location of contact marks (Note 1).

10. Copper plate as in Step 8 (Solution D) 10 minutes.

11. Rinse in tap water in overflowing tank.

12. Nickel plate (Solution E) 10 minutes, 40 amp/ft^2, pH $4.2 \pm$, 130-135 F.

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13. Nickel-cobalt alloy plate (Solution F) (Note 2), 10 minutes, 40 amp/ft^2, pH 3.5, 120-125 F.

14. Rinse.

15. Nickel plate (Solution E) - same as in Step 12.

16. Porous nickel plate (Solution G), 10 minutes, 100 amps/ft^2. minimum, pH 2.0 to 2.1, 150 F.

17. Rinse and dry.

Note 1. Panels were handled with a clean wet rubber glove during reracking.

Note 2. Two separate rectifiers were used with equal current loads for supplying current to nickel anodes on one anode bar and cobalt anodes on the other anode bar. Equal current on the two anode materials maintained the composition of the bath for depositing a 50 percent cobalt-nickel alloy.

Procedure B. Incorporating A Fused Tin Coating

The stepwise procedure for plating one panel at a time was as follows:

1.A Die Cast Panels
    Vibratory Finish

1.B AZ-31 Sheet
    Scrub with powdered pumice and brush to remove ink marking and other surface soils.

2. Soak in alkaline cleaner (Solution A) 7 minutes, 170 ± 5 F.

3. Rinse in tap water in overflowing tank.

4. Soak in activator (Solution B) 1.0 minutes, 85 ± 5 F.

5. Rinse in tap water in overflowing tank.

6. Soak in zinc pyrophosphate solution (Solution C) 7.5 minutes, 177.5 ± 2.5 F, pH 9.6 to 9.9 electrometric.

7. Rinse in tap water in overflowing tank.

8. Copper plate (Solution D)

   Enter with current on 4 minutes at 5 amp/ft^2,
   16 minutes at 10 amp/ft^2.

9. Rinse in tap water.

10. Dip in 2 percent by weight of sulfuric acid.

11. Rinse in tap water.

12. Nickel plate (Solution H), 12 minutes, 50 amp/ft^2.

13. Rinse in tap water.

14. Tin plate (Solution J)

15. Rinse and dry.

16. Heat flow the tin (Solution K), 5 to 10 seconds,
    490 - 500 F.

17. Quench in cold water.

18. Cathodic clean (Solution L)

19. Nickel strike (Solution M)

20. Rinse in tap water.

21. Nickel plate as in Step B-12.

22. Rinse in tap water.

23. Porous nickel plate, as in Step A-16.

24. Rinse and dry.

Solution Compositions Used In Procedures A and B

Solution A. Cleaner

Sodium hydroxide (NaOH)	60g/ℓ
Sodium phosphate ($Na_3PO_4 \cdot 12H_2O$)	30g/ℓ
Temperature	175 F

Solution B. Activator

Phosphoric acid (85 percent)	200mℓ/ℓ
Ammonium bifluoride (NH_4HF_2)	100g/ℓ
Temperature	75 F

Solution C. Zinc Displacement Coating

Zinc sulfate ($ZnSO_4 \cdot 7H_2O$)	48g/ℓ
Sodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$)	200g/ℓ
Lithium fluoride (LiF)	3g/ℓ
pH range	9.6 to 9.9
pH preferred	9.8

Solution D. Copper Plate

Copper cyanide (CuCN)	- 35 to 45g/ℓ
Sodium cyanide (NaCN)	- 45 to 60g/ℓ
Sodium carbonate (Na_2CO_3)	- 30g/ℓ
Rochelle salts	- 45g/ℓ
Free sodium cyanide	- 10g/ℓ

Solution E.

Nickel sulfate ($NiSO_4 \cdot 6H_2O$)	330g/ℓ
Nickel chloride ($NiCl_2 \cdot 6H_2O$)	40g/ℓ
Coumarin	1.2mℓ/ℓ
AG-4	1.2mℓ/ℓ
pH	4.0 to 4.4

Solution F.

Nickel sulfate ($NiSO_4 6H_2O$)	250g/ℓ
Cobalt sulfate ($CoSO_4 \cdot 7H_2O$)	17.5g/ℓ
Nickel chloride ($NiCl \cdot 6H_2O$)	40g/ℓ
Boric acid (H_3BO_3)	40g/ℓ
Wetting agent AG-4*	1.2mℓ/ℓ

Solution G.

Nickel sulfate ($NiSO_4 \cdot 6H_3O$)	330g/ℓ
Nickel chloride ($NiCl_2 \cdot 6H_2O$)	45g/ℓ
Boric acid (H_3BO_3)	40g/ℓ
Activated carbon Darco G-60*	15g/ℓ

Solution H.

Nickel sulfate ($NiSO_4 \cdot 6H_2O$)	330g/ℓ
Nickel chloride ($NiCl_2 \cdot 6H_2O$)	45g/ℓ
Boric acid (H_3BO_3)	35g/ℓ
Wetting agent AG-4*	25mℓ/ℓ

Solution J.

Potassium stannate ($K_2SnO_3 \cdot 3H_3O$)	210g/ℓ
Potassium hydroxide (KOH)	22.5g/ℓ
Temperature	160 - 180 F
Current density, amp/ft^2	30
Thickness, mils	0.25

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* Product of Harshaw Chemical Company, Cleveland, Ohio.

Solution K.

    Palm Shield No. 7 oil, Product of The Ironside

    Company, Columbus, Ohio.

Solution L.

Enthone cleaner Enbond 160	50g/ℓ
Temperature	180 F

Solution M.

Nickel chloride ($NiCl_2 \cdot 6H_2O$)	240g/ℓ
Hydrochloric acid (37 percent by weight)	120mℓ/ℓ
Current density, amp/ft^2	100
Time, minutes	2
Temperature, F	100

Other Plating Baths and Plating Conditions

Semi-Bright Nickel Containing Sulfur

Composition

Nickel sulfate ($NiSO_4 \cdot 6H_2O$)	330g/ℓ
Nickel chloride ($NiCl_2 \cdot 6H_2O$)	45g/ℓ
Boric acid (H_3BO_3)	35g/ℓ
Sodium saccharin ($C_7H_4NNa \cdot O_3S \cdot 2H_2O$)	0.15g/ℓ
Wetting agent AG-4	2.5mℓ/ℓ
Coumarin saturated	about 3g/ℓ

Conditioning

Temperature	120 to 130 F
pH	4.0
Current density, amp/ft^2	30

Cobalt

Composition

Cobalt sulfate ($CoSO_4 \cdot 7H_2O$)	250g/ℓ
Boric acid (H_3BO_3)	28g/ℓ

Conditions

Temperature	75 F
pH	4.0
Current density, amp/ft^2	20

Tin-Nickel Alloy

Composition

Stannous chloride ($SnCl_2$)	48g/l
Nickel chloride ($NiCl_2 \cdot 6H_2O$)	300g/l
Ammonium bifluoride (NH_4HF_2)	56g/l
Ammonium hydroxide	for pH adjustment

Condition

Temperature	150 F
pH	2.5
Current density, amp/ft^2	25

APPENDIX C

DOUBLE ZINC-COPPER PROCEDURE FOR COVERING CONTACT MARKS

APPENDIX C

DOUBLE ZINC-COPPER PROCEDURE FOR COVERING CONTACT MARKS

(1) Solvent clean

(2) Chemical pickle and rinse

Chromic trioxide (CrO_3)	180g/ℓ
Ferric nitrate ($Fe(NO_3) \cdot 9H_2O$)	40g/ℓ
Potassium fluoride ($KF \cdot 2H_2O$)	5g/ℓ

2-3 minutes at 75 F

(3) Alkaline clean and rinse

(4) Chemical activation and rinse

Phosphoric acid ($85\% H_3PO_4$)	200mℓ/ℓ
Ammonium bifluoride (NH_4FHF)	100g/ℓ

1-2 minutes at 75 F

(5) Double give displacement precoat and rinse

Zinc sulfate ($ZnSO_4 \cdot 7H_2O$)	48g/ℓ
Sodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$)	200g/ℓ
Lithium fluoride (LiF)	3g/ℓ
Sodium carbonate (Na_2CO_3)	3 - 5g/ℓ
pH	9.8 ± 0.3

10 + 5 minutes at 160± 5F with

intermediate step-activate as Step 4.

(6) Copper plate (~0.2 mil) and rinse

Copper cyanide ($CuCN$)	42g/ℓ
Potassium cyanide (KCN)	68g/ℓ
Sodium fluoride (NaF)	21g/ℓ
Hydrofluoric acid (HF) to pH	9.5±0.4

5 - 10 amp/ft^2 at 134 ± 5F

(7) Rerack

(8) Zinc plate (< 0.1 mil) and rinse

    (a) Zinc displacement bath Step 5 cathodic for ~ 10 minutes at less than 1 amp/sq ft.

    (b) Zinc pyrophosphate bath.

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Zinc oxide (ZnO)	5-1/2g/ℓ
Potassium pyrophosphate ($K_4P_2O_7$)	400g/ℓ
Sodium sulfate (Na_2SO_4)	20g/ℓ
Sodium fluoride (NaF)	12-1/2g/ℓ
Sodium bicarbonate ($NaHCO_3$)	20g/ℓ
Sodium carbonate (Na_2CO_3)	80g/ℓ
pH	10.0±0.1

Cathodic for ~/min at 5 -10 amp/ft^2.

(9) Copper plate (~ 0.2 mcℓ) and rinse

Same as Step (6)

(10) Overplate nickel or another metal.